

PATENT SPECIFICATION
DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Improvements in or relating to Cells for the Storage and
Recovery of Electrical Energy

We, SIEMENS AKTIENGESELLSCHAFT, a German Company, of Berlin and Munich, Germany and VARTA AKTIENGESELLSCHAFT, a German Company, of Frankfurt-on-Main, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to a hydrogen-oxygen cell for the storage and recovery of electrical energy.

It is known from U.S. Patent Specification No. 3,201,282 that the gases, i.e. hydrogen and oxygen formed in the electrolysis of water can be electrolytically evolved and stored with the aid of so-called "valve electrodes". These "valve electrodes" comprise a coarse-pored, operating layer, at which electrolytic evolution of gas takes place, and a fine-pored covering layer interposed between the coarse-pored, operating layer and the electrolyte. The electrolyte is advantageously KOH in hydrogen-oxygen fuel cells. Materials suitable as components of the fine-pored covering layer are electrically conductive materials which have a high overvoltage for the gas to be evolved by electrolysis for example, copper is well suited as a covering layer material in hydrogen valve electrodes. Using these valve electrodes, the gases evolved in electrolysis can be compressed to super-atmospheric pressures of several atmospheres gauge relative to the electrolyte which is under atmospheric pressure.

As the coarse-pored operating layer, there is advantageously employed in hydrogen valve electrodes, the so-called Double-Skeleton Catalyst material, abbreviated hereinafter to DSK material, which material comprises a skeleton of nickel derived from nickel carbonyl

in which Raney nickel is incorporated. A noteworthy feature of such hydrogen valve electrodes is that they are suitable both for the electrolytic evolution and subsequent dissolution, of hydrogen, that is to say, they may be employed in cells in which both electrolysis and subsequent recombination of the gases formed by the electrolysis are carried out.

In theory, valve electrodes can also be employed as oxygen electrodes in storage cells; however, difficulties arise in the choice of material for the operating layer because the optimum properties for electro-chemical evolution and subsequent dissolution of oxygen are not present in combination in one material. Thus, for example, Raney nickel is very suitable as a catalyst for the electrolytic evolution of oxygen because of its low polarisation, but it is not equally suitable for the subsequent dissolution of oxygen. As is known, the electrochemical production of oxygen is much better catalysed by silver than by nickel.

In order to combine the advantages of nickel and silver in an electrode of oxyhydrogen fuel cells, it has been proposed in German Patent Specification 1,200,903 to employ Raney Nickel and Raney silver in combination in the form of DSK material in the oxygen electrode. One disadvantage of such an electrode, however, is that, despite the low oxygen overvoltage at the nickel, silver is dissolved in the alkaline electrolyte during the evolution of oxygen; thus, the useful life of the oxygen electrode is considerably reduced. Reference is also directed to our co-pending Application No. 54188/66 (Serial No. 1144237), which discloses a hydrogen-oxygen electrochemical cell comprising a hydrogen electrode operable on both sides and two oxygen electrodes disposed one on each side of the hydrogen electrode, one oxy-

[Price 4s. 6d.]

gen electrode being nickel and operable as an anode and the other being silver and operable as an oxygen cathode.

An object of the present invention, is to 5 provide cells having improved output density and being less expensive relative to existing cells suitable for storage and recovery of electrical energy.

According to the present invention there 10 is provided a cell for the storage and recovery of electrical energy, utilising oxygen, hydrogen and an electrolyte as reactants, which comprises a hydrogen valve electrode, an oxygen diffusion electrode for dissolution of oxygen and an ion-permeable electrode, at which electrolytic evolution of oxygen occurs, interposed between the oxygen diffusion electrode and the hydrogen valve electrode.

Advantageously, the electrolyte is potassium 20 hydroxide.

As the ion-permeable electrode at which evolution of oxygen occurs according to the present invention, a metal gauze or perforated metal sheet, the surface of which has been activated by appropriate pretreatment may be employed. The pre-treatment may be carried out, for example, by spraying on to the surface, with the aid of a plasma jet, powder consisting of an aluminium-nickel alloy and 25 thereafter dissolving out of the nickel alloy the aluminium with KOH. In one embodiment of the present invention the metal gauze or perforated metal sheet is comprised solely of nickel. It is essential to prevent closure 30 of the apertures in the gauze or in the perforated metal sheet; if closure of the apertures occurs ion transport through the electrode is suppressed. The size and number of apertures is preferably chosen so that the 35 resistance of the electrode during the recombination of the stored gases to form electrical energy, in which the electrode constitutes to some extent a diaphragm, remains low. The surface of the metal gauze or perforated metal sheet may be activated by the application 40 of Raney nickel.

The ion permeable electrode can also comprise a skeleton or gauze of a plastics material the surface of which has been activated by the 50 application thereon of Raney nickel.

In accordance with a particularly preferred embodiment of the present invention, there is employed as the ion-permeable electrode a waffle metal sheet having apertures therein; such an electrode readily ensures not only the 55 passage of the ions, but also the circulation of the electrolyte perpendicularly thereto and the maintainence of the necessary spacing between the hydrogen valve electrode and the oxygne diffusion electrode.

A metal gauze or network can be provided on both sides of the ion-permeable electrode to support adjacent electrode covering layers.

65 In the case of metallic covering layers, these

gauzes or networks must be of a type capable of preventing short circuiting and must consist of insulating material, for example a plastics material.

There is advantageously employed as support for the catalyst of the oxygen dissolution electrode a material which is stable in KOH, advantageously nickel, but gauzes or skeletons consisting of a plastics material, e.g. PVC or polyamides, are also suitable.

In the cell according to the present invention, there is employed as the hydrogen valve electrode and the gas diffusion electrode one of the known electrodes suitable for the proposed purpose.

In accordance with one embodiment of the present invention the coarse-pored operating layer of the hydrogen valve electrode comprises Raney nickel. The fine-pored covering layer can comprise an electrically non-conductive material or an electrically conductive material, for example copper, the hydrogen overvoltage of which is such that no appreciable electrolytic evolution of hydrogen can take place. The covering layer is employed merely to prevent the separation of hydrogen and to render possible the adjustment of the three-phase boundary.

The operating layer of the gas diffusion electrode for the dissolution of oxygen can consist of Raney silver. In order that the three-phase boundary necessary for the generation of energy may be established, the oxygen dissolution electrode can also consist of a double-layer electrode, in which case the fine-pored covering layer can consist either of a metal or of a non-conductor. The use of asbestos paper has proved particularly advantageous.

For a better understanding of the invention and to show how the same may be carried into effect, reference will now be made, by way of example, to the accompanying drawings in which Figures 1, 2, 3 and 4 show diagrammatically four embodiments of a cell in accordance with the present invention.

Figure 1 illustrates a cell according to the present invention comprising the three electrodes arranged in accordance with the invention. A hydrogen valve electrode 1 is composed of a coarse-pored operating layer 4 and a fine-pored covering layer 5, and a gas diffusion electrode 2 for the dissolution of oxygen is composed of an operating layer 6 and of a covering layer 7. The ion-permeable electrode 3 at which oxygen is evolved can consist either of a nickel gauze or of a perforated nickel sheet. Advantageously, the surface of the electrode 3 is activated by the application thereon of a layer of Raney nickel 3a. A hydrogen gas space is denoted by 8 and an oxygen gas space for the electrodes 1 and 2 by 9. The oxygen is supplied to the gas space 9 through the duct 10, and the oxygen evolved in the electrolysis is car-

ried away together with the electrolyte through the duct 12. The hydrogen is supplied and led away through the duct 11 and the electrolyte is fed into the cell through the pipe 13.

There are denoted by 14 and 15 in Figure 1 supporting gauzes which, in the case of an electrically-conductive covering layer 5, for example copper, consist of a plastics material. The gauzes 14 and 15 are desirably incorporated into the cell when covering layers of low mechanical stability, for example asbestos paper, are employed.

If, instead of compact, for example pressed, operating layers, layers of pulverous material, for example Raney nickel powder, are employed in the electrodes, the covering layers are supported by fine and coarse gauzes (16, 17) consisting of metal or a plastics material, in which case the coarse gauzes simultaneously ensure the maintenance of the gas spaces in the assembly of cells.

The operation of a storage battery consisting of cells according to the present invention will be illustrated with reference to Figure 2.

In Figure 2 the hydrogen valve electrodes are denoted by 20, the oxygen diffusion electrodes by 21 and the ion-permeable electrodes at which evolution of oxygen takes place by 22. As in Figure 1, the electrodes 20 and 21 consist in each instance of an operating layer and of a covering layer. There are denoted by 23 and 24 hydrogen and oxygen gas spaces respectively, which in this case are associated in each instance with two like electrodes in common. Such an arrangement is particularly suitable if the cells are to be electrically connected in parallel.

If the cells of the battery are to be electrically connected in series, the gauzes employed as the supporting skeleton in the gas space (23 and 24) must consist of insulating material. The cells can also be electrically connected in series by combining a hydrogen valve electrode with an oxygen diffusion electrode and subdividing the common gas space into two spaces by means of a metal sheet or a gas-tight plate. When metal sheets are employed to subdivide the gas space they can, in combination with the supporting metal gauzes, establish electrical contact, so that bipolar electrodes according to Figure 3 are formed.

In this figure, the bipolar electrode consisting of the diffusion electrode 45, of the hydrogen valve electrode 46 and of the two gas spaces 47 and 48 is denoted by 49. The gas spaces 47 and 48 are separated from one another by the metal sheet 50 and contain the supporting metal gauzes 51 and 52. There is denoted by 53 an ion-permeable electrode similar to that of Figure 1, and by 54 a bipolar electrode in which the oxygen diffusion electrode is denoted by 55 and the hydrogen valve electrode 56.

In Figure 2, the pressure plates which hold the cells together with the aid of tie rods, are denoted by 25 and 26.

The electrolyte passes through the valve 27 into the duct 28 and is periodically or continuously circulated by the pump 29. The hydrogen formed in electrolysis passes out of the gas space 23 of the hydrogen valve electrode 20 through the duct 30 into the pressure container 31; the oxygen simultaneously evolved at the oxygen electrode 22 passes in association with the electrolyte into the gas separator 32 and passes from there through the duct 33 into the pressure container 34.

The gas space 24 of the oxygen diffusion electrode 21 communicates with the container 36 through the duct 35, the said container being in turn connected to the container 31 through the sealing liquid 37. In the storage of the gases, the valves 38, 39 and 40 are closed and the valve 41 is open. As the hydrogen pressure rises in the container 31, the air or oxygen in the container 36 is compressed to the same extent by the sealing liquid, so that the gas spaces of the hydrogen valve electrodes and oxygen diffusion electrodes are always under approximately equal pressure. This pressure is compared with the pressure in the electrolyte space 32 by means of the differential manometer 42. It must in each instance be higher than the pressure in the electrolyte space by 0.2 to 1 atmosphere gauge in the case of most electrodes.

If the pressure difference deviates from the aforesaid values in one direction or the other, the valve 38 or 39 is briefly opened by means of a regulating device until the desired value has been restored. The pressures in the containers 31 and 36 are compared by means of the differential manometer 43. When an excess pressure occurs in the container 31 because the float valve 44 closes the connecting duct, the valve 38 is automatically opened. The float valve 44 is intended to prevent hydrogen from passing from the container 31 into the container 36, which would happen, for example, if the sealing liquid were insufficient to compress the oxygen to the desired pressure in the container 36.

When it is desired to employ the installation described above for recovery of electrical energy, the valve 41 is closed and the valve 40 opened. The pressure of oxygen collected in the oxygen pressure container 34 is thereby made equal to the pressure of the hydrogen in the container 31. In addition, the pressure difference set up, on consumption of the gases, between the gas spaces 34, 36 and 31 on the one side and the electrolyte space 32 on the other side is regulated by the differential manometer 42.

The operation of gas diffusion and valve electrodes is determined by the pressure difference between the gas and electrolyte spaces. Where the electrolyte space is under atmos-

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pheric pressure, the storage of the gases has hitherto been possible only up to an absolute pressure of 4 atmospheres when two valve electrodes, one hydrogen and one oxygen valve electrode, had been employed. However, when the arrangement according to the present invention which comprises one ion-permeable electrode in the electrolyte space is employed, both the gas spaces and the electrolyte space are under increasing pressure during electrolytic operation, the necessary pressure difference between the gas spaces and the electrolyte space being maintained. Conversely, during the recombination of the stored gases, the pressure in the gas spaces gradually falls until the gases are completely consumed, the pressure in the electrolyte also falling as a result of valve control, while the necessary difference in relation to the gas spaces is again maintained. Therefore, a further noteworthy feature of the present invention is that the gases may be stored up to substantially higher absolute pressures than those mentioned above, while, in contrast to normal pressure electrolysis, the same arrangement also effects the recombination of the gases and consequential supply of electrical energy.

Figure 4 illustrates an electrical circuit arrangement for the cell illustrated in Figure 1. In this figure, 57 denotes the oxygen anode, 58 the oxygen cathode and 59 the hydrogen valve electrode. When the switch is in the position denoted by B, the storage cell operates as an electrolytic cell, when the switch is in the position A it acts as a fuel cell.

WHAT WE CLAIM IS:—

1. A cell for the storage and recovery of electrical energy, utilising oxygen, hydrogen and an electrolyte as reactants, which comprises a hydrogen valve electrode, an oxygen diffusion electrode for dissolution of oxygen and an ion-permeable electrode, at which electrolytic evolution of oxygen occurs, interposed between the oxygen diffusion electrode and the hydrogen valve electrode.
2. A cell as claimed in Claim 1, wherein the electrolyte is KOH.
3. A cell as claimed in Claim 1 or 2, wherein the ion-permeable electrode comprises a metal gauze or a perforated metal sheet, the surface of which has been activated by the application thereon of Raney nickel.
4. A cell as claimed in Claim 3, wherein the metal gauze or perforated metal sheet is comprised solely of nickel.
5. A cell as claimed in Claims 1 or 2, wherein the ion-permeable electrode comprises a skeleton or gauze made of a plastics material, the surface of which has been activated by the application thereon of Raney nickel.
6. A cell as claimed in Claims 3 or 4, wherein the ion-permeable electrode is a waffle metal sheet having apertures therein.

7. A fuel cell as claimed in Claims 1 to 6, wherein a metal gauze is provided on both sides of the ion-permeable electrode to support adjacent electrode covering layers. 65

8. A fuel cell as claimed in Claims 1 to 6, wherein a gauze or network of insulating material is provided on the ion-permeable electrode to support adjacent electrode covering layers. 70

9. A cell as claimed in Claims 1 to 8, wherein the hydrogen valve electrode has a coarse-pored operating layer which comprises Raney nickel, and a fine-pored covering layer. 75

10. A cell as claimed in Claims 1 to 9, wherein the operating layer of the gas diffusion electrode comprises Raney silver. 80

11. A cell as claimed in Claims 1 to 10, wherein the covering layer of the gas diffusion electrode comprises a metal or a non-conductor. 85

12. A cell as claimed in Claim 11, wherein the non-conductor is asbestos. 85

13. A battery for the storage and recovery of electrical energy, which comprises a combination of cells as claimed in Claims 1 to 12, wherein two adjacent hydrogen valve electrodes are combined to form a composite hydrogen valve electrode active on both sides, wherein two adjacent oxygen diffusion electrodes are combined to form a composite oxygen diffusion electrode active on both sides and wherein the cells are electrically connected in parallel. 90

14. A battery as claimed in Claim 13, wherein the composite electrodes are electrically insulated from each other and are electrically connected in series. 95

15. A battery for the storage and recovery of electrical energy, which comprises a combination of cells as claimed in Claims 1 to 12, wherein one hydrogen valve electrode and one oxygen diffusion electrode of adjacent cells electrically connected in series are combined to form a composite bipolar electrode, and wherein the gas spaces of the electrodes thus formed are separated by a metal sheet. 105

16. A battery as claimed in Claim 15, wherein the metal sheet establishes electrical contact in combination with the supporting metal gauzes. 110

17. A storage battery which comprises a combination of cells as claimed in Claims 1 to 12, wherein two hydrogen valve electrodes and two oxygen diffusion electrodes of adjacent, electrically series-connected cells are combined in each instance to form electrodes operating on both sides, the two electrodes being electrically insulated from one another. 115

18. A method of operating the battery claimed in Claims 13 to 18, wherein a pressure container, connected to the gas space of the hydrogen valve electrode, for the storage of the hydrogen communicates through a sealing liquid with a pressure container con- 120

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5 nected to the gas space of the oxygen diffusion electrode, and the former pressure container is connected to the pressure container for the oxygen storage on change over from electrolysis to fuel cell operation, and in that the connection of the last-mentioned container to the gas separator of the oxygen separation electrode is then interrupted.

10 19. A cell as claimed in Claim 1, substantially as hereinbefore described with reference to the accompanying drawings.

20. A battery as claimed in Claim 13, 15

or 17, substantially as hereinbefore described with reference to the accompanying drawings.

21. A method according to Claim 18 of 15 operating a battery substantially as hereinbefore described with reference to the accompanying drawings.

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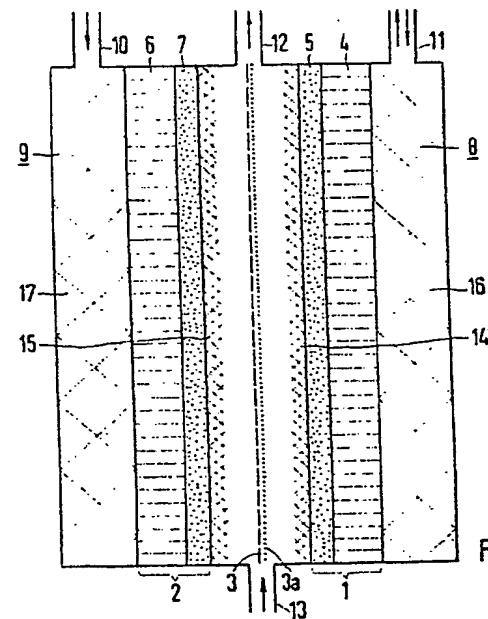


Fig. 1

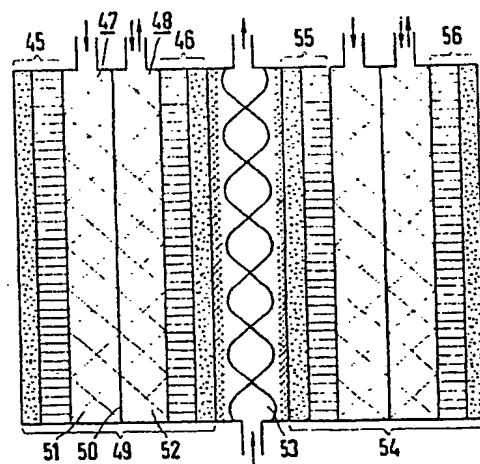


Fig. 3

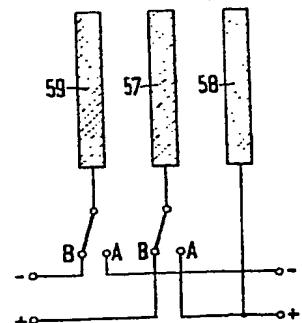


Fig. 4

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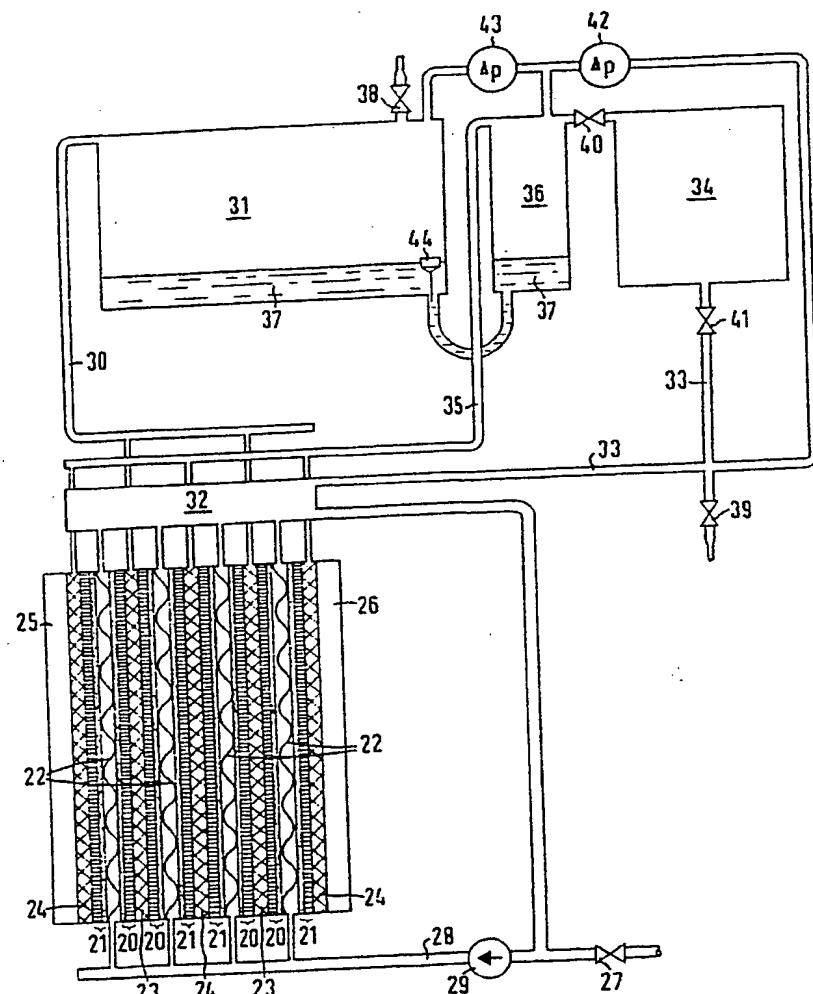


Fig.2

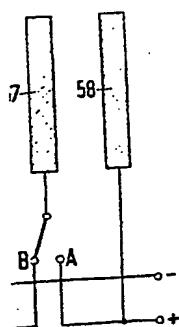
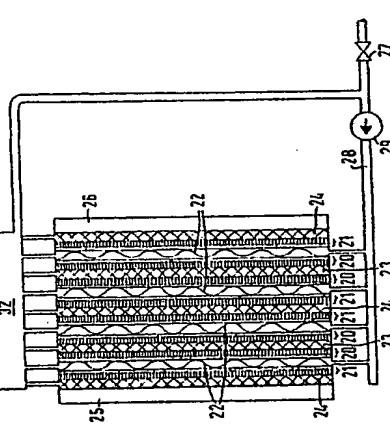
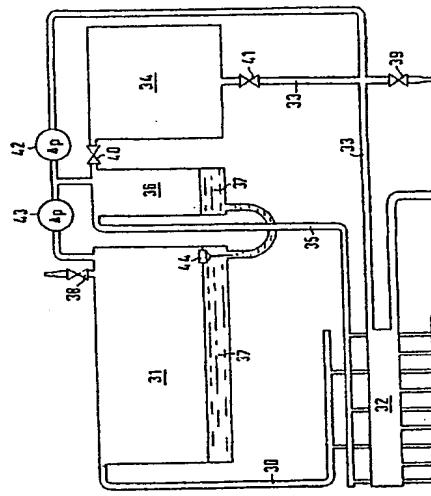
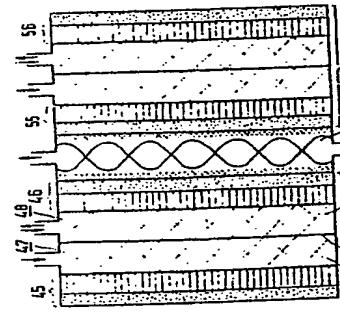
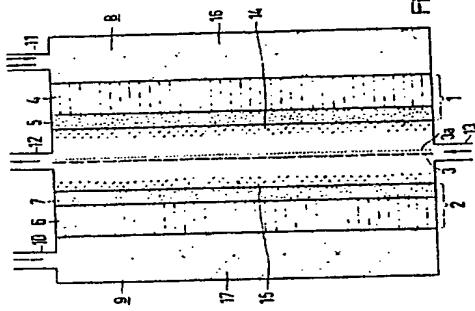


Fig. 4

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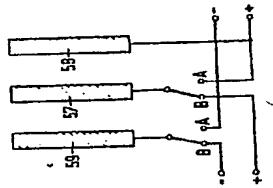


Fig.2